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(19)

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(54) PROCESS OF TREATING POROUS SUBSTRATES WITH FOAM

(71) We, UNION CARBIDE CORPORATION, of 270 Park Avenue, New York, State of New York 10017, United States of America, a corporation organized and existing under the laws of the State of New York, United States of America, (assignee of ANDREW TAINTER WALTER, GEORGE MACON BRYANT and RONALD LOUIS READSHAW), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the treatment of porous substrates, e.g. fabrics.

The treatment of textile materials with various chemicals, dyestuffs, resins and the like has been long carried out using aqueous baths in these processes. In such processes the fabric is essentially saturated by immersion in a water bath containing the treating chemical and eventually the water must be removed in order to continue the processing or to dry the fabric. Of the many procedures that have been employed in the past for the treatment of fabrics, the most commonly employed is the pad-dry process in which the fabric is immersed and saturated with the aqueous treating solution, squeezed between rollers to a given wet pick-up and subsequently dried or dried and cured on a frame or heated drying roll before being taken up in a roll once again. The amount of water retained by the fabric is normally controlled by the pressure of the squeeze roll; in conventional methods a lower limit of about 50 to 70 per cent water based on the weight of the fabric is still retained, depending upon the particular fabric used. This large amount of water requires a tremendous amount of energy in the form of heat to dry the fabric. It has been estimated that the amount of energy required to remove the water and dry the fabric is many times greater than the amount of energy that is needed in heating the cloth to carry out the desired chemical treating step, as for example, in the application and cure of a wash and wear finish on the fabric, or in the continuous dyeing of a fabric. In addition to the pad-dry process, in which the water is removed by squeezing between rollers, other procedures have recently been developed for more efficient removal of water. In one such procedure the saturated fabric is conveyed to a jet squeezer which employs a stream of compressed air jetting outward at the point of contact between the fabric and the nip rolls to substantially reduce the moisture content of the fabric. The use of this technique has resulted in a decrease of the water content in the fabric to about half of that normally remaining when using the squeeze roll technique discussed above. In another procedure vacuum extractor rolls are used. This process entails conveying the wet fabric as it exits from the treating bath over a perforated roll within which a vacuum is created whereby the moisture is extracted from the fabric. In some instances, roller coating methods can be used which continuously deliver aqueous treating composition to the fabric, with the add-on governed by the fabric speed and the rate of delivery of the treating composition by the coating roller. In this procedure the treating composition generally remains predominately on or near the surface of the fabric, particularly when low add-ons are involved.

Within the past few years, several new approaches have been made to obtain uniform application of compositions to porous substrates. These recently developed procedures use foams in different form. However, the methods by which the foams had been applied to treat the fabric or yarn leave much to be desired.

One such disclosure is to be found in U.S. 3,697,314, issued October 10, 1972. In this patent there is shown a method for producing foam and then passing a yarn through the foam so as to coat the exterior surface of the yarn with the foamed treating agent. It stresses that the yarn must pass through the foam agglomeration in order to assure a uniform distribution of the agent over the entire circumferential surface of the yarn as it passes through the foam and shows no means by which the foam could be applied on only one surface of a fabric or material and still obtain uniform distribution or uniform penetration of the interior of the yarn or fabric. An earlier attempt to use foam for the treatment of textile materials is to be found in U.S. 1,948,568, issued February 27, 1934. In this disclosure, a textile material is suspended in a closed container and foam is pumped into the container and forced through the textile material until the textile material is uniformly impregnated from all sides throughout the substrate structure and saturated with the textile treating agent in the form of a foam. In the batch process disclosed in this patent, the textile material is in a stationary or fixed position.

Though a few disclosures do exist on the use of foam for the treatment of textile materials, essentially all of the industry still uses aqueous treating baths and processes in which the fabrics are generally immersed in the bath for the application of the treating material to the textile. As previously indicated, this entails the use of a large amount of energy to subsequently remove the water from the fabric.

According to the present invention there is provided a method of treating a porous substrate by the application to the surface thereof of a functional treating composition comprising functional treating chemical compound, e.g. from 5 to 75 weight percent of functional treating chemical compound, foaming agent, e.g. from 0.2 to 5 weight percent of foaming agent, wetting agent, e.g. from 0 to 5 weight percent of wetting agent, and water, said method comprising the steps of:

(a) foaming said functional treating composition to produce a foam having a foam density of from 0.005 to 0.3 gram per cc, an average bubble size of from 0.05 to 0.5 millimeter and a foam half-life determined as hereinafter described of from 1 to 60 minutes,

(b) continuously conveying the foamed functional treating composition to an applicator nozzle, and

(c) continuously conveying the substrate across and in contact with said applicator nozzle so as to simultaneously contact said substrate with said foamed functional treating composition and said applicator nozzle at a rate such that the machine contact time is equal to or less than the equilibrium contact time, whereby a predetermined, controlled amount of said foamed functional treating composition is deposited on the surface of said substrate at said applicator nozzle, said foamed functional treating composition breaks on contact with the substrate and is readily absorbed thereby.

This invention provides a method for treating porous substrates such as a fabric or textile material or paper product by the application thereto of a functional treating composition in foam form. The invention comprises the steps of foaming a metered quantity of the functional treating composition to a foam having a specified foam density and bubble size and a specified foam stability half-life, continuously conveying the foamed functional treating composition to an applicator nozzle and continuously passing a substrate to be treated, e.g. a substantially dry textile material, across and in contact with the applicator nozzle so as to simultaneously contact the substrate with the foamed functional treating composition and the applicator nozzle. In this manner, a predetermined and controlled amount of the foamed functional treating composition is absorbed by the substrate at the applicator nozzle; the amount being, for example, an amount that leaves the surface of the substrate essentially dry to the touch. Subsequently the substrate is recovered and further treated if necessary. The process may, for example, be employed with a substrate that has not been dried before the foamed functional treating composition is applied to its surface. In this manner, drying after conventional fabric preparation steps prior to chemical treatment can be avoided.

The process of this invention can be used to treat any porous substrate such as a textile fabric or a non-woven material, paper, or wood veneer, with any of the functional treating chemical compounds that are normally used in their treatment. Thus, it can be used to apply a flame retarding composition, a waterproofing or water repellant composition, a latex, a fabric softener, a lubricant, a hand builder, a dye or pigment for coloring the substrate, a sizing agent, a whitening agent or

fluorescent brightener, a bleach, a binder for a non-woven fabric, a scouring agent, a radiation curable or polymerizable monomer or polymer or oligomer, or any other material that is normally used or applied to a fabric or similar substrate. As previously indicated, the process of this invention permits one to apply the functional treating chemical compound to the surface of the substrate without employing unnecessarily large quantities of water. In view of the escalating energy costs and short supplies of natural gas and other fuels this is a distinct advantage since less energy is required in the further and subsequent treatment of the treated substrate.

In the process of this invention a functional treating composition (hereinafter also referred to by the terms "formulation" and "formulated composition"), containing the functional treating chemical compound that is used to treat the substrate to impart a desired physical or chemical property thereto is foamed in a foaming apparatus. These functional treating compositions are used to produce the foams applied to the substrate by the process of this invention and contain the foaming agent, functional treating chemical compound and water as identified and in the concentrations hereinafter set forth. The formulated composition may also optionally contain a wetting agent and/or other additives. The equipment used for producing a foam is well known and many different types are commercially available. The formulation, in the form of a foam, is then conveyed to a foam applicator nozzle where it is transferred to the surface of the substrate that is to be treated. The manner in which the foam is transferred to the substrate is critical for uniform distribution on to the substrate. It has been found that the manner in which the transfer is made, the specific density and bubble size, and the stability of the foam are important. When this process is properly carried out, one obtains a substrate which has been treated uniformly and which may, for example, be essentially dry to the touch. Many other advantages exist over the conventional prior methods in which the substrate is completely immersed in the treating solution. For example, in the present process, the low water pick-up results in lower energy consumption in drying, reduced water consumption and water pollution, absence of migration of the functional treating chemical compounds deposited on the substrate during the drying operation, the ability to treat one side of the substrate without affecting the other side of the substrate if desired more efficient utilization of the functional treating chemical compounds, sequential addition of various functional treating chemical compounds without an intermediate drying step, as well as many other advantages which will become apparent hereinafter.

The foam is usually generated in commercially available foam generating devices, which generally consist of a mechanical agitator capable of mixing metered quantities of a gas such as air and a liquid chemical composition containing the functional treating chemical compound that is to be applied to the substrate and converting the mixture to a foam. It has been found that the density of the foam, its average bubble size and the stability of the foam are important factors for the proper operation of this invention. The foam density ranges from 0.005 to 0.3 gram per cc, preferably from 0.01 to 0.2 gram per cc.

The foams have an average bubble size of from 0.05 to 0.50 millimeters in diameter and preferably from 0.08 to 0.45 millimeters in diameter. The foam half-life is from one to sixty minutes, preferably from three to forty minutes.

The foam density and foam half-life are determined by placing a specified volume of the foam in a laboratory graduated cylinder of known weight, a 100 cc or 1,000 cc cylinder can be used, determining the weight of the foam in the cylinder, and calculating the density from the known volume and weight of the foam in the cylinder.

From the measured foam density and volume, and the known density of the precursor liquor, the liquor volume which would equal one-half of the total weight of the foam in the cylinder is calculated. The half-life is the time for this volume of liquid to collect in the bottom of the cylinder.

The foam bubble size is measured on a sample of foam taken at the applicator nozzle and is determined by coating the underside of a microscope glass slide with the foam, placing the slide on the microscope, supporting the slide at each end by two slides, and photographing it at once, preferably within 10 seconds, with a Polaroid camera at a magnification of 32 fold. In an area of the photomicrograph measuring 73 by 95 mm, corresponding to an actual slide area of 6.77 square millimeters, the number of bubbles is counted. The average bubble diameter size in mm. is then determined by the equation:

$$\text{Average Bubble Size} = \frac{2}{\sqrt{\pi}} \left[\frac{(6.77)\ (\text{Liquid Density} - \text{Foam Density})}{\text{No. of Bubbles}} \right]^{1/2}$$

The formulated compositions used for producing the foam contain a foaming agent, e.g. at a concentration of 0.2 to 5 weight percent, preferably from 0.4 to 2 weight percent; the functional treating chemical compound at a concentration, e.g. of from 5 to 75 weight percent, preferably from 10 to 60 weight percent, this being dependent upon the particular functional treating chemical compound being employed; and water. There can also be present, as an optional ingredient, a wetting agent, e.g. at a concentration of from about 0.001 to 5 weight percent or more, preferably from about 0.01 to 1.0 weight percent of the total composition when the wetting agent is used. However, it need not always be present and can in some instances be completely absent when the foaming agent supplies sufficient wetting action.

As foaming agent, one can use any surface active agent which will produce a foam having the characteristics herein before described. The formulated composition is foamed in a conventional foaming apparatus to produce a foam using air or any inert gaseous material. The amount of inert gas that is used to foam the composition is generally about 5 times the volume of the liquid composition that is to be foamed and can be as much as 200 times or more thereof. In this manner there is produced a foam having the desired density and bubble size. The particular components used to produce the foam are important in order to achieve a foam which will be readily absorbed in a uniform manner by the substrate material and permit the application of the desired amount of the functional treating chemical compound.

Illustrative of suitable foaming agents, one can mention the ethylene oxide adducts of the mixed C_{11} to C_{15} linear secondary alcohols which contain from about 10 to 50 ethyleneoxy units, preferably from about 12 to 20 ethyleneoxy units in the molecule. One can also use the ethylene oxide adducts of the linear primary alcohols having from 10 to 16 carbon atoms in the alcohol moiety, or of the alkyl phenols wherein the alkyl group has from 8 to 12 carbon atoms, wherein the adducts can have from about 5 to about 50, preferably from about 7 to 20 ethyleneoxy units in the molecule. Also useful are the fatty acid alkanolamides such as coconut fatty acid monoethanolamide. Another suitable class of foaming agents is the sulfosuccinate ester salts such as disodium N - octadecylsulfosuccinate, tetrasodium N - (1,2 - dicarboxyethyl) - N - octadecylsufosuccinate, diamyl ester of sodium sulfosuccinic acid, dihexyl ester of sodium sulfosuccinic acid, dioctyl ester of sodium sulfosuccinic acid, and the like. In addition to the above nonionic and anionic surfactants one can also use a cationic surfactant or an amphoteric surfactant such as distearyl pyridinium chloride, N-coco-beta-aminopropionic acid (the N-tallow or N-lauryl derivatives) or the sodium salts thereof, stearyl dimethyl benzyl ammonium chloride, the betaines or tertiary alkylamines quarternized with benzene sulfonic acid. These are well known and any such material can be used in addition to those specifically identified above. Blends of one or more surfactants are often used to advantage. In selecting the foaming agent for a particular formulation, care must be exercised to use those which will not unduly react with the other reactants present or interfere with the foaming or treating process.

As previously indicated a wetting agent can also be optionally present when its presence is needed to produce a foam of the desired fast breaking and wetting properties with sufficient stability to be pumped from the foam generator to the applicator nozzle. The foams are semi-stable and fast wetting and are produced from compositions containing the defined components in relatively high concentration when compared to aqueous treating compositions heretofore used. The stability of the foam produced with these compositions must allow pumping of the foam from the foam generator to the applicator head, but the foam must be readily broken and rapidly absorbed when it reaches the substrate surface. The foam breakdown characteristic is important, since retention of the foam or bubble structure on the treated substrate surface can result in craters, spotting, or otherwise uneven distribution on the substrate. In addition, foam breakdown characteristics are important to facilitate recycle; any of the known physical techniques, i.e. elevated temperature, can be used in the recycle step. In regard to

foam breakdown, the foams having the half-life defined have been found to possess the desired combination of stability to facilitate pumping and delivery to the substrate, and instability to facilitate fast wetting when contacted with the substrate and ease of recycle.

The presence of the optional wetting agent is important when the foaming agent used produces a stable foam but is a relatively poor wetting agent with the consequence that the foam does not provide sufficient front to back uniformity for continuous high speed application to the substrate. In such instances a combination of foaming agent and wetting agent is used and illustrative of suitable wetting agents one can mention the adduct of 6 moles of ethylene oxide with trimethyl nonanol, the adducts of about 7 or 9 moles of ethylene oxide with the mixed C_{11} to C_{15} linear secondary alcohols or with the C_{10} to C_{16} primary alcohols, the adduct of 9 moles of ethylene oxide with nonylphenol; the silicone wetting agents of the structure

$$(CH_3)_3SiO\left[\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ CH_3\end{array}\right]_n\left[\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ C_3H_6O(C_2H_4O)_pR\end{array}\right]_m Si(CH_3)_3$$

wherein n has a value of 5 to 25, m has a value of 3 to 10, p has a value of 6 to 20 and R is alkyl of 1 to 6 carbon atoms; also useful are the commercially available fluorocarbon wetting agents such as the known perfluoroalkylated surfactants.

The amount of such wetting agent to be added to provide for the fast breaking and rapid absorption properties will vary depending upon the particular wetting agent selected and this amount can be readily ascertained by a preliminary small scale evaluation. Thus, it was observed that the concentration of the fluorocarbon wetting agents is preferably in the range of from 0.001 to 0.5 weight percent, and the range for the silicone wetting agents is preferably from 0.01 to 0.3 weight percent. It has also been observed that excessive quantities of the silicone of fluorocarbon wetting agents may inhibit foam formation or shorten foam stability to such an extent that pumping and delivery of foam to the substrate is no longer feasible. Thus, the preliminary small scale screening test will establish if such a problem exists in any particular instance. As previously indicated, some foaming agents possess sufficient wetting properties that there is no need for the use of the supplementary or optional wetting agents. However, in most instances, better front to back uniformity of treatment is obtained using a mixture or combination of foaming agent and wetting agent. It has also been observed that the addition of a known foam stabilizer, such as hydroxyethyl cellulose, hydrolyzed guar gum, can be of benefit, provided it does not unduly affect the desired foam properties.

The process of this invention can be used to apply any number of functional treating chemical compounds to a substrate to impart a particular property or treatment thereto. Thus, the process can be used to apply flame-retarding reagents, waterproofing or water-repellant reagents, mildew proofing reagents, bacteriostats, permanent press or wash and wear compositions, softeners, lubricants, hand builders, dyes, pigments, sizes, whitening agents, fluorescent brighteners, bleaches, binders for non-woven fabrics, latexes, scouring agents, thermal or radiation curable monomers or oligomers or polymers, soil or stain release agents, or any other material known to be used in the treatment of textiles or papers. An important requirement of the selected functional treating chemical compound is that it not interfere with the foam generation, nor with the foam properties to the extent that the foamed formulation could not be properly conveyed to the applicator nozzle or that the foam could not be properly applied to the substrate in a manner and form that it would rapidly break and penetrate the substrate in a uniform manner. The process is not limited to any particular functional treating chemical compound or combination of compounds. Illustrative of typical functional treating chemical compounds one can mention dimethyloldihydroxyethylene urea, dimethylolethylene urea, dimethylolpropylene urea, urea formaldehyde resins, dimethylol urons, the methylolated melamines, methylolated triazones; the methylolated carbamates such as the ethyl or methoxyethyl or isopropyl or butyl carbamates; the epoxides such as vinyl cyclohexene dioxide, 2,3-diallyoxy-1,4-dioxane, 2,3-bis(2,3-epoxypropoxy)-1,4-dioxane, the diglycidyl ether of bisphenol-A, bis(3,4-epoxybutyl)ether; flame-

proofing agents such as tetrakis hydroxymethyl phosphonium chloride, polyvinyl chloride latexes, (N-hydroxymethyl-3-dimethyl phosphono)propionamide water-proofing or water repellant agents such as aluminum formate, sodium formoacetate, methylene bis-stearamide; mildew proofing and bacteriostat agents such as copper-8-quinolinolate, dihydroxydichlorodiphenylmethane, zinc salts of dimethyldithiocarbamic acid, dihydroxymethyl undecylenamide; latexes such as polyvinyl acetate latexes, acrylic latexes, styrene-butadiene latexes; softeners such as emulsifiable polyethylene, dimethyl stearate ammonium salts; lubricants such as butyl stearate, diethylene glycol stearate, polyethylene glycol, polypropylene glycol; hand builders such as polyvinylacetate latexes, acrylic latexes, styrene-butadiene latexes; dyes and pigments such as Acid Blue 25 (Color Index 62055), Acid Red 151 (Colour Index 26900), Direct Red 39 (Color Index 23630), Dispersed Red 4 (Color Index 60775), Phthalocyanine Blue 15 (Color Index 74160); sizes such as polyvinyl alcohol, corn starch; whitening agents such as 4-methyl-7-dethylaminocoumarine; bleaches such as sodium hypochlorite, chlorine, hydrogen peroxide, dichlorodimethyl hydantoin sodium perborate; binders for non-woven fabrics such as ethylenevinyl acetate emulsion polymer, acrylic emulsion polymer, vinyl-acrylic copolymer; scouring agents such as sodium lauryl sulfate, triethanolamine lauryl sulfate, sodium N-methyl-N-oleoyltaurate, primary and secondary alcohol ethoxylates radiation curable monomers and oligomers such as 2-hydroxyethyl acrylate, neopentyl glycol diacrylate, pentaerythritol triacrylate, isodecyl acrylate, acrylated epoxidized soybean or linseed oil; antistatic agents such as ethoxylated stearyl amines; soil or stain release agents such as acrylic polymers, fluorocarbon emulsions.

The compositions used in the process of this invention are prepared by mixing the selected functional treating chemical compound, foaming agent and water, with, if used, water and/or other conventional agents normally present, for example in the amounts indicated. This formulation for example has a Brookfield viscosity of from 0.5 to 75 cps, preferably from 1 to 50 cps at 25°C. The manner of preparing the formulation will depend upon the particular functional treating chemical compound present and the procedures normally used for preparing compositions containing the selected functional treating chemical compound are normally employed in producing our formulations. The formulation is then foamed, the foam is conveyed to a foam applicator device or nozzle and there it is applied to the surface of the substrate.

In producing the foam, a metered quantity of the formulation is introduced to the foamer and foamed. The foaming step is controlled by adjusting the volume of air introduced to the foamer and the rotation rate, in rpm, of the rotor in the foamer. The rotor's rotating rate plays an important role in producing a foam that will have the previously defined bubble size and half-life. The relative rates of feed of the formulation and the gas will determine the density of the foam.

The nozzle used to apply the foam to the substrate and the manner in which the substrate contacts the nozzle play important roles in the successful operation of this process. The applicator nozzle is designed that it has sufficient side-to-side width that foam can be applied across the width of the substrate. The gap or width between the forward and back lips of the nozzle orifice will vary from 10 mils to about six inches or more, preferably from 20 mils to 4 inches. The width or gap of the nozzle orifice is of a dimension such that the machine contact time is equal to or less than the equilibrium contact time for the particular foam-substrate combination that is being run, as defined by the equation $MCT \lesssim ECT$.

The machine contact time, abbreviated MCT, is the amount of time that any given point of the substrate remains over the nozzle orifice during the foam treatment. The machine contact time in seconds is equal to the gap or orifice width in inches divided by the speed of the substrate in inches per second. The equilibrium contact time, abbreviated ECT, is a measured characteristic property of the foam/porous substrate operative system. It is a measured value for each operative system and is the measured time value required for a particular foam/porous substrate system, the porous substrate moving at a selected speed, to uniformly absorb the foam at the rate it is being delivered to the applicator nozzle at atmospheric pressure.

Additional foam will be absorbed by the substrate when the foam is under pressure. Preferably, a slight uniform pressure of 2 to 20 inches of water is maintained to control uniformity of application. It has been observed that when MCT is greater than ECT that non-uniform application results. In other words,

when absorption rate is greater than the delivery rate of the foam, uniform application is no longer achieved. It has been observed that in such instances one may obtain an uneven stripe or random pattern across the width of the substrate.

The nozzle orifice preferably consists of two lips, edges or surfaces that are spaced apart and are of sufficient length to essentially equal the width of the substrate. The substrate contacts the edges of the two lips, which may be of any selected configuration, e.g. pointed, tapered, flat, beveled, arced, or otherwise, with a pressure sufficient to provide a seal and confine the foam to the zone between the lips. The angular relationship between the substrate as it makes initial contact with a lip and as it exits from a lip, with the application zone, and with the lip surfaces are varied over a wide range, to assure a seal between the substrate and lips. The extremities of the orifice must be sealed so that the foam does not escape. In some instances when MCT=ECT, it has been possible to operate with only the exiting or downstream lip in contact with the substrate.

A figurative description of an embodiment of the invention is described in the accompanying drawing, which illustrates the typical relationship that exists between foam uptake by the substrate and hydrostatic pressure on the foam. The curve describes the uptake of foam, measured as total composition including water, by a nominal 4 oz./yd.^{2}, 65/35 polyester/cotton sheeting fabric at a machine contact time (MCT) of 0.025 second. It is surprising and unexpected to find such a large volume of foam being taken up by the fabric at atmospheric pressure within the very short contact time of 0.025 second. The figure shows that foam equivalent to 8 percent of the weight of the substrate, or approximately 35 percent of the unoccupied volume of the fabric, is taken up by the substrate at atmospheric pressure within this short machine contact time. It is also apparent from the slope of the curve that the uptake of foam by the substrate can be increased substantially at low hydrostatic pressures. Uptake of foam by the substrate can also be increased at longer equilibrium contact time. It has been found that the uptake is relatively independent of fabric speed so long as the nozzle orifice width is adjusted to maintain the same machine contact time. On the other hand, the uptake is affected by fabric and foam characteristics as described elsewhere. At low levels of uptake (below 8 weight percent in Figure 1) an unsteady condition is encountered which leads to nonuniform application of functional treating chemical compounds; i.e., the MCT is greater than ECT. A steady state condition can be achieved when MCT=ECT as illustrated by the intercept of the curve and the abscissa in the figure. Control over uniformity of uptake is achieved with a positive hydrostatic pressure. Therefore, the machine contact time is adjusted to be equal to, or preferably less than the equilibrium contact of the fabric-foam system. Preferred operating conditions are achieved when the machine contact time causes a hydrostatic pressure on the foam in the nozzle ranging between 2 in. and 10 in. of water pressure.

The process of this invention permits the application of a single functional treatment, or multiple functional treatments, using a plurality of foaming and application systems, to a substrate followed by subsequent drying or drying and curing of the foam treated substrate prior to take-up. Further, since the amount of foam composition added on to the substrate is generally below the water retention capacity of the substrate, the substrate can be rolled up without drying and stored or transferred to another location for subsequent use or treatment. The substrate to which the foam is applied may be, but need not be, dry. The ability to apply a desired quantity of a foam composition independent of the initial state of dryness of the substrate, provided the substrate is not completely saturated, is a unique, unexpected, unobvious, and desirable feature of this process.

The multiple application of two or more treatments or components in succession, using separate functional treating compositions and applicator nozzles for each, with or without intermediate drying, curing or take-up steps is within the scope of this invention. This multiple application procedure is of particular advantage when the separate treatments or functional treating chemical compounds are not compatible with each other or are too reactive with one another to be present in a single formulation.

The substrate to which the foamed formulation has been applied can be subsequently thermally or radiation treated dependent upon the particular formulation applied and the objective sought. Thus, the treated substrate can be thermally treated to dry or to cure the applied composition or it can be exposed to non-ionizing or ionizing radiation. In any instance any of the known thermal or radiation treatments pertinent to the particular formulation can be employed.

Thus, for drying or thermal cure one can use infrared lamps, hot gases, ovens, heated rollers, or similar conventional heating means. For radiation curing one can use ultra-violet radiation, gamma radiation, electron beam radiation, or similar conventional means, whether inerted or not.

The rate of foam composition uptake by the substrate is influenced by the foam properties, the weight and construction of the substrate, the initial degree of dryness of the substrate and the degree of hydrophilicity of the substrate. Thus, the natural fibers such as wool, cotton or linen are known to be more hydrophilic than are some of the synthetic fibers such as polyester. Hence, these natural fibers can absorb more of the foamed formulation and still maintain an essentially dry-to-the-touch feel. It has also been observed that selective pre-wetting or post-wetting of localized areas of the substrate results in migration of the treating foam composition outward towards the edges of the pre-wetted or post-wetted regions, while the non-wetted regions will dry uniformly without migration. With a dye-containing foam composition, this technique produces washed-out patterns similar to the effects achieved by tie-dyeing procedures without the need to tie the substrates.

A particularly unexpected and unobvious finding was that the foam was absorbed by the substrate at a rapid rate and in large volume. In most instances the desired amount of foamed formulation was applied and absorbed within a period of a fraction of a second, generally within less than 0.05 second. Equally unexpected was the discovery that the foam could be applied evenly across the entire substrate or in selected patterns.

In a typical embodiment the equipment used would consist of equipment means to convey the substrate, e.g. fabric, from a let-off roll to the applicator nozzle, a reservoir to prepare and store the formulated composition, foam generating means for foaming said composition, foam recycle means, means to convey the foam to the applicator nozzle, a foam applicator head and nozzle and take-up means. Optionally one can include treating means to treat or cure the foam treated substrate, such as an oven or a radiation generating source. For the purposes of this application the foam applicator nozzle was produced using plexiglass sheet so that visual observation could be maintained. However, any other construction material could be used.

In a typical operation, described with reference to the use of a fabric as the substrate, a fabric was conveyed from a let-off roll across various guide rolls and nip rolls and the foam composition was applied to one of the surfaces of the fabric as the fabric made contact with the nozzle of the foam applicator head. The fabric was then collected at a take-up roll. As the fabric was conveyed across the foam applicator nozzle, the foamed functional treating composition came into contact with it and was absorbed by the fabric. The foam entered the chamber via the foam inlet point in the base and exited from the foam applicator head via the applicator nozzle slit whereupon it was deposited on the fabric. The foam was produced by foaming a metered quantity of the functional treating composition in a commercially available foamer and conveying the formed foam to the chamber of the applicator head by suitable conveying means. As the foam entered the chamber via the foam inlet point and filled it, foam velocity diminished before it entered the slit or orifice of the applicator nozzle. It was observed that uniform coating of the foam onto the fabric substrate was achieved when both lips of the applicator nozzle were preferably in contact with the fabric. If the first or upstream lip did not touch the fabric, foam would tend to build up behind the applicator nozzle lip producing a bank of foam and non-uniform application and penetration would often result. When the second or downstream lip of the applicator nozzle did not touch the fabric the curtain of foam would be pulled away from the nozzle slit and areas of the fabric would be skipped, also leading to non-uniform application of the foam composition. In view of these observations it was determined that uniform application of the foam to the fabric substrate could best be accomplished when both lips of the applicator nozzle were preferably in contact with the fabric substrate. In some instances it was possible to achieve good application with the fabric in contact solely with the downstream lip, particularly when ECT=MCT.

The following equations are useful in determining the amounts of formulated composition metered into the foamer and the amount of foam applied to the substrate. Equation I indicates the amount of liquid formulated composition metered in cubic feet per minute:

I $$V_l = \frac{(C_s)(v_s)(w_s)(\lambda)}{(c_l)(\rho_l)}$$

Equation II indicates the amount of foam applied to the substrate in cubic feet per minute:

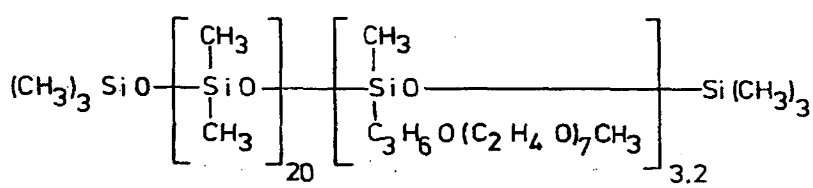
II $$V_f = \frac{(C_s)(v_s)(w_s)(\lambda)}{(c_l)(\rho_f)}$$

The symbols have the following meanings:
v_s=substrate linear velocity (line speed), ft/min
V_l=liquor volume flow rate, ft^3/min
V_f=foam volume flow rate, ft^3/min
ρ_f=density of foam, lb/ft^3
c_l=concentration (solids of liquor, % ows (on weight of solution)
w_s=substrate weight, lb/ft^2
c_s=solids add-on to substrate, % owf (on weight of substrate)
λ=width across treated substrate or nozzle orifice, ft
ρ_l=density of liquid formulated composition, lb/ft^3

The equipment used in Examples 1 and 2 consisted of an Oakes Mixer, Model No. 4MHA, connected to a foam applicator head. "Oakes" is a Trade Mark. A metered quantity of the formulation was introduced to the mixer, foamed and conveyed to the applicator via suitable conduits.

The foam applicator head consisted of a chamber and a nozzle. The chamber had a length of about 12 inches, a width of about 1.5 inches and a height of about 1 or 1.5 inches. In the center of the base of the chamber there was located a foam inlet point through which the foamed textile treating composition entered the chamber. Mounted on the top of the chamber was the nozzle that had an elongated slit or orifice running the length of the chamber; the slit could be adjusted in width. In this particular instance it had a height of about 1.5 inches. The lips of the slit tapered outwardly and downwardly at an angle of about 45°. Two foam applicator heads were used differing in the size and shape of the chamber to which the nozzle was affixed. The first applicator head had a chamber volume of 390 cc measuring about 12×1.5×1.5 inches. The second applicator head had a triangular configuration when viewed from the front with a chamber volume of about 84 cc. In this instance the base of the applicator head tapered at an angle from the center where the foam inlet means were located at a depth of one inch to a zero height at the ends of the chamber.

Silicone Wetting Agent I has the formula:



The test procedures used were:

Wrinkle recovery	AATCC 66—1959T
Tear strength	ASTM D—1424—59
Tensile strength	ASTM D—1862
Wash-wear	AATCC 124—1967T Washing Procedure III; Drying Procedure A and B
Yellowness Index	Using a Hunterlab Model D—40 Reflectometer

$$\text{Yellowness} = \frac{\text{Green reflectance} - \text{Blue reflectance}}{100}$$

The present invention will now be further illustrated by way of the following

examples. In the examples, the foams from formulations not identified as being comparative possess a foam density of from 0.005 to 0.3 gram per cc, an average bubble size of from 0.05 to 0.5 millimeter and a foam half-life of from 1 to 60 minutes. Also in the examples, the substrate used was continuously conveyed across and in contact with the applicator nozzle so as to simultaneously contact the substrate with the foam and the applicator nozzle at a rate such that the machine contact time is equal to or less than the equilibrium contact time (i.e. MCT<ECT).

Example 1

A wash-wear formulation was prepared containing the following components:

DMDHEU	2,210 g.
Zinc nitrate, 30%	492 g.
Softener I	246 g.
Foaming Agent I	32.4 g.
Wetting Agent I	12.4 g.
Silicon Wetting Agent I	3 g.
Direct Red 37, C.I. 22240	3.5 g.

DMDHEU—1,3-dimethylol-4,5-dihydroxy-2-imidazolidone, 45% aqueous solution
Softener I—aqueous emulsion of low molecular weight polyethylene 30% solids
Foaming Agent I—adduct of mixed C_{11}—C_{15} linear secondary alcohols with 20 moles of ethylene oxide
Wetting Agent I—adduct of mixed C_{11}—C_{15} linear secondary alcohols with 9 moles of ethylene oxide

The above textile treating composition was foamed in the commercially available Oakes Mixer. The foam produced was conveyed to the foam applicator heads described above and applied to a cotton fabric passing over the slit of the foam applicator nozzle at a speed of about 25 feet per minute to obtain a chemicals add-on of about 9 weight percent. The width of the slit in the foam applicator nozzle was varied; the details of this series of experiments is set forth in Table A below.

TABLE A

Applicator Head		Foam Producing Conditions			
Chamber Size cc	Slit Width in.	Press. psig	Speed RPM	Foam Density gm/cc	Foam Penetration
84	.015	32	Med	0.056	Poor
84	.035	32	Med	0.056	Poor to Fair
390	.010	32	Med	0.056	Excellent
390	.030	32	Med	0.056	Excellent
84	.015	30	Med	0.046	Poor
84	.035	30	Med	0.046	Poor
390	.010	30	Med	0.046	Excellent
390	.030	30	Med	0.046	Excellent
84	0.015	32	Max	0.050	Poor
84	0.015	12	Max	0.116	Excellent

Example 2

A wash-wear textile treating composition was prepared similar to that described in Example 1, but omitting the Silicone Wetting Agent. The textile treating composition had a solids content of 39.8 weight percent. It was foamed in a manner similar to that described in Example 1 to produce a foam having a foam density of between 0.05 and 0.06 gram per cc. This foam was applied to mercerized cotton broadcloth in the manner described in Example 1 with the fabric moving at a speed of 25 feet per minute over the nozzle. The nozzle slit was 25 mils wide and the chamber volume was 390 cc. The solids add-on of the foam composition to the fabric was between 6 and 7 weight percent. After the application of the foamed composition to the textile fabric the textile fabric felt dry to the touch. The foam treated fabric samples were stored in a plastic bag until samples were removed for curing. At that time, swatches of the foam treated fabric were cured without an intermediate drying step on pin frames for periods of 10, 30, 60 and 90 seconds at temperatures of 320° and 360°F. In addition, at each temperature one sample was

initially separately dried for 90 seconds at 300°F. and then cured for an additional 90 seconds at the indicated curing temperature treatment. Thus, the resulting samples compared a flash curing, that is without an intermediate drying step at various times and temperatures, with a series of samples in which the foam applied finish was initially dried and cured by the conventional procedures. The results achieved are summarized in Table B. From the results it is shown that good wash-wear performance properties are obtained by the process of this invention wherein continuous foam application is used to apply the wash-wear treating formulation to one surface of the fabric. It can also be observed that the intermediate drying step is not necessary to obtain good wash-wear performance properties and that such properties can be obtained in a short curing step at an appropriately high temperature of about 360°F. for about 30 to 60 seconds. The wash-wear properties of the treated fabrics showed excellent durability of the applied reactant as evidenced by the fabric properties measured after 20 home laundering treatments.

TABLE B

Treatment		Properties							After 20 Home Launderings	
Cure Temperature °F.	Cure Time SECS.	Dry Wrinkle Recovery DEG.	Wet Wrinkle Recovery DEG.	Tear Strength G.	Tensile Strength g.	Wash-Wear Tumble dry	Wash-Wear Spin dry	Yellowness Index	Dry Wrinkle Recovery deg.	Wash-Wear Tumble Dry
320	10	.166	180	2112	27	1.1	1.2	.036	182	1.0
	30	253	183	1856	21	1.5	2.8	.037	204	2.2
	60	267	188	1616	17	2.9	2.4	.036	247	3.2
	90	265	234	1520	17	3.3	3.1	.038	251	3.4
	Control*	279	222	1248	19	3.7	3.7	.039	254	3.5
340	10	190	189	2160	26	1.2	1.2	.037	183	1.2
	30	246	211	1680	19	2.8	2.4	.039	222	3.0
	60	259	218	1552	17	3.1	2.4	.042	227	3.0
	90	286	222	1376	18	3.3	2.8	.041	253	3.4
	Control*	278	225	1520	18	3.2	2.6	.044	244	3.2
360	10	227	178	2112	23	2.0	1.6	.036	176	1.3
	30	279	240	1520	20	3.0	1.8	.040	208	2.3
	60	286	247	1200	15	3.5	3.1	.045	261	3.5
	90	288	247	1232	14	3.6	3.3	.043	261	3.5
	Control*	274	253	1264	15	3.4	2.9	.042	273	3.4

*Control indicates samples were dried 1.5 minutes at 300°F. and cured at indicated cure temperature for 1.5 minutes to typify conventional curing conditions. All samples other than these marked control were not thermally dried.

Example 3

A wash-wear formulation was prepared containing the following components, in weight percentages:

DMDHEU	80.4%
Zinc nitrate, 30%	17.9%
Foaming Agent I	1.2%
Wetting Agent I	0.4%
Silicone Wetting Agent I	0.1%

The liquid formulation included a trace amount of a commercial tracer dye, it had a density of 1.18 g/cc and a total solids of 43.5 weight percent. It was foamed in a commercially available Ease-E-Foamer Model No. E1000 at a ratio of 16 volumes of air per volume of liquid and the thick foam produced had a density of 0.073 g/cc. Foam was produced at a feeding rate of 564 cc/min. of the liquid formulation to the foamer. The pressure on the foamer head was 20 psig. The foam was delivered to an applicator nozzle and uniformly applied to one surface of a 50/50 polyester/cotton sheeting about 9 inches wide that weighed about 4 ounces per square yard. The fabric was travelling over the applicator nozzle at a speed of 300 feet per minute for an MCT of 0.0011 second. Under these application conditions the pressure drop of the foam at the nozzle was 16.5 inches of water pressure drop across the fabric with an eight percent chemicals add-on of the formulation to the fabric.

The equipment used in the process consisted of suitable feed, take-up and guide rolls for the fabric; the foamer and means for delivering the foam to the applicator head; and the applicator head. The applicator head comprised a chamber having a foam inlet point centrally located in the base and the applicator nozzle mounted on the top. The internal chamber dimensions of the applicator head were about 9.5 inches long by about 1.75 inches wide by about 2 inches high, representing a total volume of about 33 cubic inches. The applicator nozzle consisted of a two-piece slotted head forming a slot extending along the length of the chamber. The head, attached to the chamber body, had a taper of 45° for each piece exiting from the chamber, a slot width of 0.064 inch, a slot height of 1.5 inches, and the exterior lips also had a taper of 45°. The foam entered the chamber through the inlet point in the base, filled the chamber at a positive pressure, exited from the chamber through the slot of the applicator nozzle and contacted the fabric and was absorbed by it at the applicator nozzle lips. The fabric moved across and contacted both exterior lips of the applicator nozzle at the indicated speed of 300 feet per minute. Uniform application on the fabric was observed.

Example 4

A wash-wear formulation was prepared containing the following components, in weight percentages, and a tracer dye:

DMDHEU	76.0%
Zinc Nitrate, 30%	15.1%
Softener I	7.6%
Wetting Agent I	0.3%
Foaming Agent I	0.9%
Silicone Wetting Agent I	0.1%

The liquid formulation had a density of 1.18 g/cc and a total solids content of 43.5 weight percent and also contained a tracer dye. It was foamed using the same equipment described in the immediately preceding example at a ratio of 25 volumes of air per volume of liquid formulation; the foam produced had a density of 0.048 g/cc. The pressure on the foamer head and lines to the applicator head was 18 psig. The foamed formulation was applied to one surface of a 65/35 polyester/cotton sheeting fabric that was 48 inches wide and weighed about 4 ounces per square yard using modified commercially available tenter frame and feeder means to convey the fabric across the foam applicator nozzle and subsequently cure the formulation. Fabric speed was maintained at 30 feet per minute for an MCT of 0.011 second. To insure proper cure in the pilot scale pin tenter dryer, a limitation on the speed was imposed by the equipment. Contact time in the tenter frame dryer was 42 seconds at 360°F. Tension on the fabric was maintained by nip roll and idler roll means. Improved results were noted in this experiment when idler rolls were located on each side of the applicator nozzle slot

about 6 inches below the top of the applicator nozzle lips and about 12 inches from the center of the nozzle orifice. The add-on of foamed chemical formulation was eight percent.

The apparatus used was a larger version similar to that described in Example 3 and contained a distribution plate in the internal chamber. The inside chamber dimensions were 60 inches long by 2.25 inches wide by 7 inches high at the foam inlet end and 5 inches high at the opposite end. The distribution plate was located across the entire width and length of the chamber, at a point 4 inches from the top of the chamber. This distribution plate had 61 openings, each 0.07 inch in diameter, uniformly located throughout its surface and divided the applicator head into a lower distribution chamber and an upper application chamber. The foam entered the distribution chamber at the end having the greatest height, passed through the openings in the distribution plate into the application chamber to give a uniform rise of the foam into the application chamber and then through the applicator nozzle to the fabric surface. The slot in the applicator nozzle was 0.032 inch wide and 2 inches high. Under the conditions stated, the pressure drop of the foam across the distribution plate was 4 inches of water pressure. It was observed that a uniform application of the foamed formulation was obtained.

Example 5

A formulation was prepared containing the following components in weight percentages:

DMDHEU	80.4%
Zinc Nitrate, 30%	17.9%
Foaming Agent I	1.2%
Wetting Agent I	0.4%
Silicone Wetting Agent I	0.1%

The liquid formulation included a tracer dye, it had a density of 1.18 g/cc and a total solids of 43.5 weight percent. This formulation was foamed by several different procedures using different commercially available foam producing equipment. An Oakes mixer, Model 4MHA, was used running the rotor at 1,740 rpm and a pressure of 30 psig and then at 740 rpm and a pressure of 16 psig to produce foams having a density of 0.09 g/cc. The liquid formulation was fed at the rate of 564 cc/minute and the ratio of air to liquid was about 13:1 by volume. It was observed that the bubbles produced when the foamer was operated at 740 rpm were larger than those when operated at 1,740 rpm. The second commercially available foamer used was the Ease-E-Foamer, Model M 1000, operated at 410 rpm and a pressure of 20 psig; this produced a foam having a density of 0.092 g/cc. The foam bubbles produced in this instance were slightly larger than those produced using the Oakes Mixer. The foams were applied to one surface of a 65/35 polyester/cotton sheeting fabric by the procedure described in Example 3 using the same application equipment therein described. The nozzle slit width was one inch. The fabric was travelling over the applicator nozzle at a speed of 300 feet per minute for an MCT of 0.0167 second. Application uniformity was superior with the bubbles produced using the Ease-E-Foamer and the bubbles produced using the Oakes Mixer operated at 740 rpm. Some non-uniformity was observed on application of the bubbles produced with the Oakes Mixer operated at 1,740 rpm; this non-uniformity was attributed to the smaller bubble size obtained.

Example 6

A formulation was prepared containing the following components in weight percentages:

DMDHEU	81.2%
Zinc Nitrate, 30%	17.9%
Wetting Agent II	0.6%
Foaming Agent I	0.3%

Wetting Agent II —adduct of mixed C_{11} to C_{15} linear secondary alcohols with 7 moles of ethylene oxide.

The liquid formulation had a density of 1.18 g/cc. and a total solids of 43.5 weight percent. It was foamed using a commercially available Ease-E-Foamer operating at 410 rpm at ratios of 10, 13 and 20 volumes of air per volume of liquid.

The foams produced had the densities indicated in Table III. The foam was delivered to an applicator nozzle and uniformly applied to the surfaces of three different fabrics, a 65/35 polyester/cotton (Fabric A), a 50/50 polyester/cotton (Fabric B) and a 100 percent cotton (Fabric C) at an add-on of 6 weight percent. In this series the rate at which the fabric was travelling was varied at 100, 200 and 300 feet per minute over the applicator nozzle to determine the balance point between ECT and MCT at wide orifice openings. In addition, the width of the slit of the applicator nozzle was varied from ¼ inch to 4 inches using modified applicator heads. At these applicator nozzle slit widths, it was found that good application was obtained under these specific conditions. It was also observed that the foam begins to roll in the applicator nozzle and develops a rolling bank at high speeds and wide nozzle openings, as well as a change in the foam structure.

The applicator heads used in this example were constructed so that the width of the applicator nozzle could be varied over a wide range. The basic structure was similar to that described in Example 4 in that it consisted of a distribution chamber and an application chamber separated by the distribution plate at a height of one inch above the base. Applicator Head A had a distribution chamber measuring 9 inches long by 1 inch in height by 3 inches in width and an application chamber measuring 9 inches long by 3 inches in height with the width adjustable from 0.25 to 3 inches. The distribution plate had 17 holes each 3/8 inch in diameter. In Application Head B the distribution chamber was 6 inches wide and the application chamber could be adjusted up to six inches in width; this head had the same number and size of holes. The nozzle width was equal to the selected adjusted width of the application chamber and selection was made by adjusting the location of one of the lips, the two lips forming two sides of the application chamber. Applicator Head B was used when the nozzle width was greater than 3 inches. During application of the foamed formulation to the fabric, the fabric was in contact with both lips of the applicator nozzle. The conditions under which the fabrics were treated are summarized in the following table wherein the nozzle slit width and water pressure are reported:

TABLE III

Nozzle Slit Width Inches and (Water Pressure Inches)

Fabric	At 100 fpm	At 200 fpm	At 300 fpm	Density g/cc
A	1/4(—)	1/4 (1/4)	3 (1/4)	0.12
B	1/4 (3/4)	1/2 (1)	3 (5/8)	0.12
C	1/2 (2)	1/4 (1)	3 (1 1/2)	0.12
A	1/4 (1)	1/4 (2 1/4)	3 1/4 (1 1/2)	0.09
B	1/2 (3/2)	1/2 (1 1/2)	3 1/4 (1 3/8)	0.09
C	3/4 (2)	3/4 (1 5/8)	3 1/4 (1 3/4)	0.09
A	1/2 (1 1/2)	1 1/2 (1 1/2)	4 (5/8)	0.06
B	3/4 (5/8)	1 1/2 (1 1/4)	4 (1)	0.06
C	1 (2)	1 1/2 (1 1/2)	4 (1/4)	0.06

Example 7

A wash-wear formulation was prepared containing the following components in weight percentages:

DMDHEU	81.2%
Zinc Nitrate, 30%	17.9%
Wetting Agent II	0.6%
Wetting Agent I	0.3%

The liquid formulation had a density of 1.18 g/cc. and a total solids of 43.5 weight percent. It was foamed in a commercially available Ease-E-Foamer, at a ratio of 13 and 6 volumes of air per volume of liquid with the foamer operated at 410 rpm. The combination of wetting agents served the dual function of foaming agent and wetting agent. Satisfactory foam was produced having a half-life of about 15 minutes and densities of 0.089 g/cc. and 0.2 g/cc., respectively. The foam was applied using an applicator head 9 inches long by 2.5 inches in height. The two sides were spaced one inch apart and the tops tapered at an angle of 45°. The space between the sides comprised the nozzle orifice or gap. Foam was introduced into

the nozzle applicator through the base and fabric was moved across the nozzle at a speed of 100 feet per minute for an MCT of 0.011 second. Excellent uniformity of application was observed.

Example 8 (Comparative)

A formulation was prepared containing the following components in weight percentages:

DMDHEU	81.2%
Zinc Nitrate, 30%	17.9%
Wetting Agent II	1.2%

Attempts to produce a foam by the procedure followed in the immediately preceding example resulted in a foam that had a density of 0.48 g/cc. The high density of this foam made it unsatisfactory and it could not be uniformly applied by the process of this invention. In this example Wetting Agent II by itself was shown not to be an adequate foaming agent.

Example 9

Two formulations were prepared as follows:

	A**	B
DMDHEU	81.2	81.2
Zinc Nitrate, 30%	17.9	17.9
Foaming Agent I	0.3	0.6
Half-life, Minutes	—	26

**=Comparative

These formulations were foamed in the manner similar to that described in Example 7. Formulation A does not produce a satisfactory foam since the density was 0.41 g/cc. Formulation B produced a satisfactory foam having a bubble size of 0.243 mm and a density of 0.04 g/cc. when the foamer was operated at 210 rpm. Using the procedure and application head described in Example 7, the foam from formulation B was applied to 50/50 polyester/cotton sheeting fabric at a 9 percent add-on at a speed of 300 feet per minute. Uniform application was achieved on the polyester/cotton. When the foamer was operated at 485 rpm, the foam produced, though it had the same density, had a bubble size of 0.043 mm., and it would not apply uniformly.

Example 10

Two formulations were prepared containing the following components:

	A	B
DMDHEU	81.2	81.2
Zinc Nitrate, 30%	17.9	17.9
Foaming Agent I	1.2	1.2
Silicone Surfactant I	0.1	—

These formulations were foamed in the manner similar to that described in Example 7. In both instances satisfactory foam was produced having a density of 0.09 g/cc. the formulation containing Silicone Surfactant I produced foam that had a foam half-life of 14 minutes, while the foam half-life of the formulation that did not contain the silicone was 10 minutes.

Example 11

Two formulations were prepared containing the following:

	A	B
DMDHEU	81.2	81.2
Zinc Nitrate, 30%	17.9	17.9
Wetting Agent II	0.6	0.6
Foaming Agent II	0.3	0.3
Zonyl FSN (Perfluoroalkyl Surfactant)	0.5	

Foaming Agent II —adduct of mixed C_n—C_{15} linear secondary alcohols with 12 moles of ethylene oxide.

Foams were produced by the procedure similar to that described in Example 7. The foam produced with formulation A had a density of 0.09 g/cc. and a half-life of 5.5 minutes. The foam produced with formulation B had a density of 0.09 g/cc. and had a half-life of 21 minutes. Application of the two foams produced on 50/50 polyester/cotton and 100 percent cotton sheeting fabric resulted in good uniform distribution of the composition. The foamed formulation was applied using the procedure and equipment described in Example 7.

Example 12

A series of formulations was prepared differing in the amount of thickener added. The constant components in the formulations were as follows:

DMDHEU	81.2
Zinc Nitrate, 30%	17.9
Wetting Agent II	0.6
Foaming Agent I	0.3

Formulation A did not contain any thickener and had a Brookfield viscosity of 5.2 cps at 23°C. Formulation B contained 0.1 percent hydroxyethyl cellulose, which in a one percent solution had an LVT Brookfield viscosity of about 3,000 cps at 25°C using a No. 3 spindle at 30 rpm; the formulation had a Brookfield viscosity of 15.7 cps at 23°C. Formulation C contained 0.2 percent of the same hydroxyethyl cellulose and had a Brookfield viscosity of 30.4 cps at 23°C. Formulation D contained 0.3 percent of the same hydroxyethyl cellulose and had a Brookfield viscosity of 83.1 cps at 23°C. These formulations were foamed as described in Example 7 to produce foams having a density of 0.045 g/cc. and the foams were applied to 4 ounce 65/35 polyester/cotton and 100 percent cotton sheeting fabrics. The applicator head used had a distribution chamber measuring 9 by 2 by 2 inches and an application chamber measuring 9 by 2 by 0.75 inches. The applicator nozzle slit was therefore 0.75 inch wide. The distribution plate had 15 holes, each 3/16 inch in diameter. The inward taper on the exit lip of the nozzle was 5°. The add-on at a fabric speed of 300 feet per minute was six weight percent. The uniformity of application was good for formulations A to C inclusive and fair for formulation D.

Example 13

A formulation was prepared containing the following components:

DMDHEU	81.2
Zinc Nitrate, 30%	17.9
Wetting Agent II	0.6
Foaming Agent I	0.3

The liquid formulation had a density of 1.18 and a total solids content of 43.5 percent. It was foamed in an Ease-E-Foamer by feeding 188 cc per minute of the formulation into the foamer with sufficient air to produce a foam that had a density of 0.02 g/cc while operating the foamer at 410 rpm. The foam was applied to the surface of a 50/50 polyester/cotton sheeting fabric at an add-on of 3 percent using the apparatus described in Example 12 at an applicator nozzle width opening of 1 3/16 inches at a 5° taper on the exit lip. Application to the fabric was at a fabric speed of 300 feet per minute and a pressure drop of 0.25 inch water pressure across the fabric. Good uniform application was achieved.

Example 14

The effect of pre-wetting the fabric with 60 percent water when using the process of this invention was evaluated in this example. A formulation was prepared containing the following components:

DMDHEU	80.9
Zinc Nitrate, 30%	17.9
Wetting Agent II	0.6
Foaming Agent II	0.6

This formulation was foamed using the Ease-E-Foamer operating at 410 rpm and a feed of 125 cc per minute. The foam produced had a foam density of 0.06 g/cc. This was applied to the pre-wet cotton sheeting using the apparatus described in

Example 12 and an applicator nozzle width opening of 0.5 inch at a fabric speed of 300 feet per minute. Uniform application of the formula was achieved on the pre-wet fabric and the pressure drop across the fabric was 0.5 inch of water pressure. When the same foam was applied to the same fabric that had not been pre-wet, the pressure drop across the fabric was 2 5/8 inches of water pressure.

Example 15

A formulation was prepared containing the following components:

DMDHEU	81.2
Zinc Nitrate, 30%	17.9
Wetting Agent II	0.6
Foaming Agent I	0.3

This formulation was foamed in an Ease-E-Foamer with the rotor operating at 410 rpm using a formulation feed of 564 cc per minute and a ratio of 15 volumes of air per volume of formulation. The foam produced had a density of 0.078 g/cc. This foam was applied to 8 ounces per square yard, 50/50 polyester/cotton fabric sheeting at a fabric speed of 300 feet per minute at an add-on rate of 4.5 percent under the same conditions described in Example 13 using a nozzle that had a slot width opening of 1 3/16 inches. Excellent uniformity was observed. The pressure drop across the fabric was 2 7/8 inches of water.

Example 16

A dye formulation was prepared containing the following:

Latyl Orange 2 GFS (C.I. 44)	6.8 lb
Water	36.4 lb
Wetting Agent II	0.4 lb
Foaming Agent II	0.4 lb

The pH was adjusted to 5—6 with acetic acid and foams were produced using the Ease-E-Foamer with the rotor operating at 340 rpm having different foam densities:

Foam	A	B
Density, g/cc	0.03	0.057
Half-life, min	—	5
Liquid feed to foamer, c/c min	125	125

The foams were applied to 100 percent polyester and to 65/35 polyester/cotton sheeting fabric using the applicator head described in Example 12 with the nozzle orifice adjusted to a gap width between the lips of 0.5 inch. The fabric was moving at a speed of 100 feet per minute across the orifice, contacting both lips of the nozzle, total wet add-on was 14 weight percent.

When applying Foam A to the 100 percent polyester, sections of the nozzle opening were blocked with tape and a striped pattern was obtained on the fabric. The foam, as in the other examples, was uniformly applied to the fabric, leaving the fabric essentially dry to the touch. After standing for a period of time, the striped fabric was heated at 420°F for 3 minutes to fix the dye. Clear definition of the pattern was obtained. In a similar manner, the entire fabric surface was dyed by removing the tape from the nozzle.

Foam A was used to apply a pattern to 65/35 polyester/cotton with the same equipment. A pattern effect was attained by positioning a stencil between the nozzle and fabric, the stencil moving at the same rate as the fabric, as the foam exited from the nozzle. The dyed areas of the fabric were uniform and even and clear definition of the dyed areas was noted.

Foam B was applied to 100 percent polyester in the same manner to completely dye the fabric. Uniform application and even dyeing were observed. A section of the fabric was sprinkled with water after the foam was applied, the fabric taken up on a roll, stored about 48 hours, and the dye was then fixed at about 420°F for 3 minutes, a random pattern was observed showing lighter areas where the water droplets were deposited.

In all instances a scour after dye fixation is recommended.

Example 17

A combination wash-wear and dye formulation was prepared containing the following:

DMDHEU	24,270 g
Zinc Nitrate, 30%	5,370 g
Wetting Agent II	180 g
Foaming Agent II	180 g
Latyl Orange 2 GFS	3,540 g

A portion of the above formulation was diluted with 25 percent water, the pH adjusted to 5—6 and a foam was produced as described in Example 16, having a density of 0.046 g/cc and a foam half-life of about 9.4 minutes, by feeding 376 cc/min of the formulation to the foamer and using an air to liquid ratio of about 25:1. The foam was applied to 65/35 polyester/cotton fabric using the equipment and orifice opening described in Example 16. The fabric was moving at a speed of 300 feet per minute, for an MCT of 0.008 second. The add-on to the fabric was 4.5 weight percent of DMDHEU and 1.5 weight percent of dye. When the fabric was entirely dyed, uniform application and even dyeing were noted. The foam-treated fabric was subsequently cured at 420°F for 3 minutes. The same foam was used to print a pattern on the cloth by the procedure described in Example 16. Clear definition was obtained. The data illustrates that one can apply several treatments, in this case both wash-wear and dyeing, simultaneously and without intermediate drying steps. Scouring after dye fixation is recommended to improve crocking and wet fastness properties, and remove any loose dye from the fabric.

Example 18

A dye formulation was prepared containing the following:

Latyl Orange 2 GFS	5.6 lb.
Water	36.4 lb.
Wetting Agent II	2.1 lb.
Foaming Agent II	0.4 lb.
Silicone Surfactant I	0.04 lb.
Hydroxyethyl Cellulose*	0.04 lb.

*Same as described in Example 12.

The pH of the formulation was adjusted to 5—6 with acetic acid and foam was produced using the Ease-E-Foamer as in Example 17. The foam had a density of 0.075 g/cc. It was applied to 65/35 polyester/cotton using the same procedures and equipment used in Example 17 for an add-on of 1.5 weight percent dye. Application uniformity was excellent and an evenly dyed fabric was obtained, both before and after dye fixation, by heating at 420°F for 3 minutes.

A portion of the dye formulation was diluted with five times its weight of water. This was padded onto the fabric and dye migration evaluated by AATCC Test Method 140—1974. For comparative purposes a swatch of the foam treated fabric, taken immediately after the foamed dye formulation had been applied to it, was also evaluated for dye migration. It was observed that the fabric treated with the concentrated dye formulation by the foam process of this invention showed essentially no dye migration, whereas the fabric treated with the diluted and padded formulation showed excessive and pronounced dye migration. The values obtained from the test procedure were 4% and 48.8%, respectively.

Attention is directed to our copending application No. 20361/77 (Serial No. 1585873) which describes and claims a foam composition for treating a porous substrate, and a method of preparing said foam composition.

WHAT WE CLAIM IS:—

1. A method of treating a porous substrate by the application to the surface thereof of a functional treating composition comprising functional treating chemical compound, foaming agent, water and optionally wetting agent, said method comprising the steps of:

(a) foaming said functional treating composition to produce a foam having a foam density of from 0.005 to 0.3 gram per cc, an average bubble size of from 0.05 to 0.5 millimeter and a foam half-life (determined as hereinbefore described) of from 1 to 60 minutes,

(b) continuously conveying the foamed functional treating composition to an applicator nozzle, and

(c) continuously conveying the substrate across and in contact with said applicator nozzle so as to simultaneously contact said substrate with said foamed functional treating composition and said applicator nozzle at a rate such that the machine contact time is equal to or less than the equilibrium contact time, whereby a predetermined, controlled amount of said foamed functional treating composition is deposited on the surface of said substrate at said applicator nozzle, said foamed functional treating composition breaks on contact with the substrate and is readily absorbed thereby.

2. A method as claimed in claim 1, wherein the foam density is from 0.01 to 0.2 gram per cc.

3. A method as claimed in claim 1 or 2, wherein foamed functional treating composition is applied to one side of the substrate.

4. A method as claimed in claim 1 or 2, wherein foamed functional treating composition is applied to both sides of the substrate.

5. A method as claimed in any one of claims 1 to 4 wherein a multiplicity of foamed functional treating compositions are applied to the substrate.

6. A method as claimed in any one of claims 1 to 5, wherein foamed functional treating composition is applied to the substrate to produce a design thereon.

7. A method as claimed in any one of claims 1 to 6, wherein the substrate is selectively pre-wet prior to application of the foamed functional treating composition thereto.

8. A method as claimed in any one of claims 1 to 6, wherein the substrate is selectively post-wet after the application of the foamed functional treating composition thereto.

9. A method as claimed in claim 1 and substantially as hereinbefore described with reference to any of Examples 1 to 7 and 9 to 18.

10. A method as claimed in claim 1 and substantially as hereinbefore described with reference to the accompanying drawing.

11. Porous substrates whenever treated by a method as claimed in any one of claims 1 to 10.

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1585874 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*